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HIGHLY REFRACTORY POROUS CERAMICS.(U)
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# FOREIGN TECHNOLOGY DIVISION

HIGHLY REFRACTORY POROUS CERAMICS

By

I. Ya. Guzman

# EDITED TRANSLATION

FTD-ID(RS)T-0206-79 14 March 1979

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HIGHLY REFRACTORY POROUS CERAMICS

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## U. S. BOARD ON GEOGRAPHIC NAMES TRANSLITERATION SYSTEM

| Block | Italic | Transliteration | Block | Italic | Transliteration |
|---|---|---|---|---|---|
| А а | *А а* | A, a | Р р | *Р р* | R, r |
| Б б | *Б б* | B, b | С с | *С с* | S, s |
| В в | *В в* | V, v | Т т | *Т т* | T, t |
| Г г | *Г г* | G, g | У у | *У у* | U, u |
| Д д | *Д д* | D, d | Ф ф | *Ф ф* | F, f |
| Е е | *Е е* | Ye, ye; E, e* | Х х | *Х х* | Kh, kh |
| Ж ж | *Ж ж* | Zh, zh | Ц ц | *Ц ц* | Ts, ts |
| З з | *З з* | Z, z | Ч ч | *Ч ч* | Ch, ch |
| И и | *И и* | I, i | Ш ш | *Ш ш* | Sh, sh |
| Й й | *Й й* | Y, y | Щ щ | *Щ щ* | Shch, shch |
| К к | *К к* | K, k | Ъ ъ | *Ъ ъ* | " |
| Л л | *Л л* | L, l | Ы ы | *Ы ы* | Y, y |
| М м | *М м* | M, m | Ь ь | *Ь ь* | ' |
| Н н | *Н н* | N, n | Э э | *Э э* | E, e |
| О о | *О о* | O, o | Ю ю | *Ю ю* | Yu, yu |
| П п | *П п* | P, p | Я я | *Я я* | Ya, ya |

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

## RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

| Russian | English | Russian | English | Russian | English |
|---|---|---|---|---|---|
| sin | sin | sh | sinh | arc sh | sinh$^{-1}$ |
| cos | cos | ch | cosh | arc ch | cosh$^{-1}$ |
| tg | tan | th | tanh | arc th | tanh$^{-1}$ |
| ctg | cot | cth | coth | arc cth | coth$^{-1}$ |
| sec | sec | sch | sech | arc sch | sech$^{-1}$ |
| cosec | csc | csch | csch | arc csch | csch$^{-1}$ |

| Russian | English |
|---|---|
| rot | curl |
| lg | log |

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| Г г | *Г г* | G, g | У у | *У у* | U, u |
| Д д | *Д д* | D, d | Ф ф | *Ф ф* | F, f |
| Е е | *Е е* | Ye, ye; E, e* | Х х | *Х х* | Kh, kh |
| Ж ж | *Ж ж* | Zh, zh | Ц ц | *Ц ц* | Ts, ts |
| З з | *З з* | Z, z | Ч ч | *Ч ч* | Ch, ch |
| И и | *И и* | I, i | Ш ш | *Ш ш* | Sh, sh |
| Й й | *Й й* | Y, y | Щ щ | *Щ щ* | Shch, shch |
| К к | *К к* | K, k | Ъ ъ | *Ъ ъ* | " |
| Л л | *Л л* | L, l | Ы ы | *Ы ы* | Y, y |
| М м | *М м* | M, m | Ь ь | *Ь ь* | ' |
| Н н | *Н н* | N, n | Э э | *Э э* | E, e |
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| cos | cos | ch | cosh | arc ch | $\cosh^{-1}$ |
| tg | tan | th | tanh | arc th | $\tanh^{-1}$ |
| ctg | cot | cth | coth | arc cth | $\coth^{-1}$ |
| sec | sec | sch | sech | arc sch | $\operatorname{sech}^{-1}$ |
| cosec | csc | csch | csch | arc csch | $\operatorname{csch}^{-1}$ |

| Russian | English |
|---|---|
| rot | curl |
| lg | log |

Highly Refractory Porous Ceramics. I. Ya. Guzman. Publisher: "Metallurgy", 1971.

There is a discussion and generalization of the literature data, practical experience and the author's own investigations relating to the technology, structure, properties and utilization of highly refractory porous materials used for heat insulation, high-temperature filters, catalyst supports and many other purposes.

It is intended for the engineers and scientists in refractory industry enterprises, design and research organizations, and related technical fields connected with the utilization of high temperatures.

42 illustrations, 53 tables, 272 references.

Guzman, Iosif Yakovlevich
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PREFACE

Sources of information about porous highly refractory materials are sufficiently numerous and diverse, yet acquaintance with them and their practical utilization are hampered by their being scattered in various domestic and foreign publications.

The purpose of the present book is to consolidate the available information, principally about highly refractory materials. To give a complete picture, there are also included in the book two small sections on fireclay and siliceous materials of ordinary refractoriness. Taking into account the relatively small size of the book, the author aimed for maximum generalization, especially in preparing the sections about production methods, structure and properties of porous refractory materials, and purposely avoided describing the technological details and also the equipment.

Being an adherent of the concept of the controlling influence of the structure of porous materials on all their properties, the author attempted to confirm this by means of practical data, constantly emphasizing the tight interrelation between production methods, structure and properties.

This being the first attempt at generalizing the data in the field of porous highly refractory materials, the book, of course, is not free from deficiencies; the author will gratefully accept all criticisms and wishes of the readers.

INTRODUCTION

The manufacture of porous refractory and especially highly refractory materials is one of the comparatively new technical fields. In the early twenties, thermally insulating refractory materials with artificially created porosity were lacking and they were used neither in Europe nor in the United States (1). Apparently the idea itself was not yet clearly formulated of using porous materials for high-temperature insulation since methods of producing porous structural materials by the introduction of combustible admixtures were known and patented almost 100 years ago (2,3).

Gaseous methods of producing porous materials became known somewhat later. A number of patents were granted in 1879-1880 for producing porous materials through the use of foaming agents and a gas formed as a result of the chemical interaction of the additives introduced into the ceramic body. At that time, however, these methods did not find practical application and only later were they used for producing porous articles basically from cementitious materials capable of setting (gypsum, cement).

The industrial exploitation of the technology of producing porous refractory materials in the Soviet Union dates back to the early thirties, when the "Mosogneupor" trust started to turn out thermally insulating refractories at local plants, using carbonaceous clay from the Moscow region in combination with sawdust (1,4,5). Orders from users for the first half of 1936 amounted to 400 tons in all, which is explained by insufficient interest on the part of the users, as it turned out later, in a notable achievement of refractory technology, and also by the low quality of the articles, narrow assortment and the absence of a sufficiently positive experience in their use.

In the following years, the production of light weight refractory materials in various countries developed at very rapid rates. Already in 1936 many brands of ~~articles~~ products were produced for use as thermal insulation at various temperatures, and also highly refractory porous materials based on corundum and magnesite were released in a limited amount.(1,6).

The technology of manufacturing effective porous fireclay refractories was developed through the efforts of the All-Union (S. V. Glebov, M. N. Genzler et al) and the Ukrainian (A. A. Pirogov) refractory institutes. With several changes, this technology is incorporated in the technology of the manufacture of the basic types of lightweight refractories turned out by contemporary industry.

Many types of products were successfully introduced to industry and their production increased rapidly enough (7). By a rough estimate, 6-8 thousand tons of lightweight refractories were produced in 1940 in this country which, however, could not satisfy the calculated demand amounting to roughly 50-60 thousand tons.

In the domestic industry, mainly the methods of introducing combustible admixtures and foaming found practical application; the method of chemical gas formation was not practiced on a large scale. Abroad, on the other hand, the latter method was used rather widely but the method of combustible admixtures remained predominant. Until 1948, the lightweight refractories obtained in this manner were formed exclusively by a plastic method (8). Then the technology was developed for producing lightweight refractories with combustible admixtures also by the semidry molding method.

The technology of the first domestic thermally insulating highly refractory materials was developed by A. A. Pirogov (9), who extended the foam method to nonplastic materials, among them highly refractory ones. Pirogov's investigations were characterized by the high standard, the depth of the study of the material and the valuable final results, which later on served as the basis for the development of the technology of new highly refractory materials. Already in this earlier work ways were contemplated of controlling the density and properties of the materials produced and the effect of the technological parameters on the process of producing highly porous thermally insulating materials was noted.

The accomplishment of the prewar years, retaining its value even today, is the development and industrial introduction by I. S. Kaynarskiy and coworkers of the technology for manufacturing lightweight silica on the basis of combustible admixtures (10, 11).

On the whole in the prewar period there was developed, industrially assimilated and perfected the technology of producing refractory porous materials on the basis of the traditional nat~~ive~~ural aluminosilicate raw materials; this process lasted approximately for a decade ~~and~~ even after the war.

In quality the new period began in the middle fifties and especially in the sixties in connection with the intensive development of high-temperature techniques associated in ~~its~~ their turn with atomic energy, rocket construction, jet-propelled aviation, high-temperature vacuum technology, etc. There appear numerous publications and patents touching upon the technology, properties and application of highly refractory porous materials principally on the basis of synthetic raw materials.

The development of the porous refractory and highly refractory materials industry follows the line of perfecting production, specialization, and designing and building shops and factories producing only lightweight refractories; the process of mechanization and automation progresses rapidly; special production lines and tunnel kilns are created that are adapted exclusively for porous products.

Along with thermally insulating and protective materials, for which the thermophysical characteristics are the most important, there are also produced other porous materials, for which the structural characteristics and the associated material properties are decisive (porosity size, dimensions, form and nature of the size distribution of the pores, permeability, etc.).

Permeable porous ceramics and ~~powder metallurgy,~~ cermets, and also filtration processes, are described in sufficient detail in appropriate monographs (12-14). Along with the usual filtering ceramics, there are also investigations in recent years of other types of ceramics with controlled structure, intended for use as porous diaphragms in scavenging molten metals, porous matrix supports for electrolytes in fuel cells, catalyst supports and in other special fields, in which permeable ceramics based on fillers of quartz sand and fireclay are as a rule unsatisfactory. In view of this, at the present time there are investigated and produced products of this type from chemically pure materials, of necessity highly refractory, capable of serving at high temperatures, high pressures, under the conditions of the action of corrosive media, etc.

A large contribution to the development of the technology of porous highly refractory materials was ~~was~~ made by the employees of the Ukrainian Institute of Refractories, the D. I. Mendeleyev MKhTI, and the All-Union Institute of Refractories; a number of studies in the development of new efficient materials of ordinary refractoriness were conducted by the employees of the Snigirev refractory plant in collaboration with other organizations.

Chapter III

## APPLICATION OF POROUS HIGHLY REFRACTORY MATERIALS

### VALUE OF POROUS REFRACTORY MATERIALS

Porous refractory materials play a very important role in contemporary technology, first of all as thermal insulation and protection.

The most completely studied application of porous materials has been as thermal insulation (1, 3, 6, 7, 17, 18). The following demands are made upon thermal insulation materials:

- minimal heat expenditure for warming up the enclosing surfaces;
- low heat losses through the walls as a result of thermal conduction;
- minimal time for heating the aggregate to the required temperature;
- small wall thickness.

Porous materials answer the indicated requirements to a considerably greater degree than dense ones thanks to the high porosity and considerably lower thermal capacity, conductivity and diffusivity.

The efficiency of uninsulated metallurgical and ceramic furnaces varies within the limits of 10 to 35% and it is even lower for forging, annealing and hardening furnaces (2 to 16%). On the contrary, in boiler plants the efficiency is considerably higher on account of the extensive application of thermal insulation and the better use of the heat of the waste gas, amounting to 60 to 80% (6, 7).

The efficiency of porous refractory materials is revealed in analyzing the heat balance of aggregates (1, 6). Heat consumption for accumulation and radiation are the basic heat losses in furnaces, reaching 80 to 90% of the whole heat consumption (1, 7).

The efficiency of materials is higher as ~~the~~ their apparent density is lower, the furnace volume is smaller, the wall thickness is greater, the heating temperature of the furnace is higher and the operating cycle of the furnace is shorter (1), i. e., this becomes especially apparent in small high-temperature periodically operated furnaces.

The high efficiency of lightweight refractories is reported in numerous publications (1, 4, 6, 7, 15, 17-19, 28, 43, 44, 66, 164, 239-241).

It is most advantageous to use thermally insulating materials for the inner lining, i. e., directly at the heat sources. In this case, the heating time, the weight and thickness of the enclosing surface and the fuel consumption are reduced since the heat losses are reduced for both accumulation and radiation. Outer insulation is sometimes even harmful since it increases the heat losses by accumulation at the **lining**, which frequently exceed the savings obtained by a reduction in heat losses from radiation by the walls (4).

The low heat capacity of ~~the~~ walls made from lightweight materials and their ability to heat and cool rapidly, i. e. the low inertia of such furnaces, create especially favorable conditions for the rapid and efficient control of their thermal conditions. However, the low heat capacity of the lining makes the furnace very sensitive to a change in the amount of fuel burned, which in some cases is not desirable. A uniform distribution of temperatures in the melting chamber is attained through the use of thermally insulating materials, i. e. stability of the production cycle is provided, the productivity of the furnaces is increased and the work conditions are improved (17, 240).

According to the data of S. V. Glebov (6), with a rational arrangement of the enclosure wall, its weight can be reduced 9 to 12 times and the heat capacity 10 to 11 times while retaining the given (permissible) loss by radiation. Under some conditions, a wall of lightweight refractory one brick in thickness can replace a wall, lined with a dense refractory, that is 3.5 bricks in thickness (1). In this case, the accumulation losses decrease more than 10 times and the overall dimensions and weight of the furnaces also decrease.

As calculations show (241), 1 ton of product with a density of 1.3 g/cm$^3$ ~~are~~ is equivalent in terms of thermal insulation properties to 3 tons of dense brick; with a density of 0.8 g/cm$^3$ to 6-7 tons and with an apparent density of 0.4 g/cm$^3$ to 18-20 tons. According to foreign data (242), the use of lightweight refractories permits a reduction of 5-10 times in the weight of the furnace lining and in the required capital investment.

Of no less value (especially for periodic furnaces) is the saving in time on account of the sharp reduction in the duration of heating and cooling. The lightweight lining is heated roughly 5 times faster than a lining of dense brick; the saving in time for heating the furnace reaches 70 to 80% with a corresponding saving in fuel (1, 19, 44).

According to US experience (18), with thermal insulation of open hearth furnaces, fuel consumption is reduced on the average by 10 to 15%. According to the data of F. Norton (17), the fuel saving in periodic furnaces amounts to 45%.

A large economic effect is attained by the use of lightweight silica and fireclay refractories in the elements of the lining of various furnaces: silica calcining, heating, periodic electric furnaces for heating steel billets, roller hearth furnaces and also in the lining of the cars in tunnel furnaces (7, 15, 19, 44, 240, 243).

Through wide testing of lightweights in various furnaces it was determined that on account of the reduction in losses to the surrounding medium and in the useless heating of the walls, the fuel saving during the firing of the products reaches 40 to 60% in periodic furnaces and 15 to 20% in continuous ones (242). In spite of the greater cost of the porous materials, the sharp reduction in the weight of the lining also provides some reduction in the construction cost of heating installations (240).

For a more complete utilization of lightweight refractories, it is necessary to increase their production, expand the assortment, increase the dimensions of individual products, continually raise their quality while reducing the apparent density, and reduce the cost. For this, as was indicated (28, 50, 66, 164, 241), it is necessary to have specialized plants, mechanization and automation of the production processes, perfection of the technology and development of new, more effective materials, increased productivity of the equipment, and a substantial reduction in the cost price of the marketable production.

Along with the unquestionable virtues, porous refractory materials have a whole series of substantial deficiencies integrally connected with its porous structure. In this case, with an increase in porosity, i. e. with an improvement in the thermal insulation properties of the material, all its deficiencies are progressively worsened (3, 6, 7, 17, 258):

low mechanical strength against any mechanical effects;

low slag resistance;

low thermal stability;

considerable reheat shrinkage (this does not apply to lightweight silica);

nonuniformity of the structure;

instability of density and therefore of the properties of the material;

high permeability;

complexity of the technology;

increased cost.

The enumerated deficiencies limit considerably the applications of porous refractory materials while in a number of cases they completely exclude their use. As a rule, they are not suitable under conditions where there is an effect of slags and other molten substances (glasses, metals, etc.), and under conditions where there is an effect of gas flows at high velocities, especially in the case of the presence of dust in the gases, resulting in abrasive action.

At the present time, we have at our disposal various highly porous materials with considerable mechanical strength, good volumetric stability at high temperatures and very high thermal stability. Still the most important problem in the field of improving the properties of porous refractory materials remains an increase in their strength and thermal stability. As for slag resistance, the solution of the problem apparently ought to be a search along the path of developing highly porous materials with micropores that are inaccessible to penetration by slags and other melts, which appears, however, to be a very difficult problem.

## APPLICATION OF POROUS REFRACTORY MATERIALS

Analysis of numerous literature data makes it possible to conclude that porous refractories are applied in two principal directions.

The first is thermal insulation, the determining factor being the thermal insulation properties, i. e. the coefficient of thermal conductivity $\lambda$ and thermal reflection; here in the case of using materials for aircraft, the apparent density $\gamma$ is also important (it is customary to consider the product $\lambda\gamma$ as the index of efficiency of the material).

The second direction comprises the areas in which the controlling property of the material is its porous structure and the properties associated with it, principally the dimensions of the pores and the resulting permeability, specific surface, etc. In this case, the thermal conductivity is generally of no importance or plays a secondary role. Porous refractory materials are used in those cases where the processes of filtration, gas distribution, impregnation of porous media, application of electrolytes, electrochemical processes, etc. are conducted at high temperatures, when other materials turn out to be unsuitable.

In some cases, porous materials must posess electrical insulation properties, chemical stability in corrosive media, among them various gases at high temperatures, have appropriate nuclear characteristics, etc. Thermally insulating refractories (for example, ultralightweight) can be used for soundproofing.

## Use of Porous Materials as Thermal Insulation

The porous refractory materials that are produced are used mainly for thermal insulation, including about 50% in ferrous metallurgy, 20% in the engineering industry and metalworking, and 30% in all other branches of technology (241). Porous refractory materials are used in those cases the temperature in the insulated unit exceeds 900-1000°C.

For thermal insulation of industrial metallurgical, ceramic and other furnaces, various types of fireclay and silica lightweights are used basically; in recent years, high alumina materials began to be used for this purpose, including fibrous ones, and sometimes porous materials from pure oxides. There is reason to assume that the role of the latter will grow with the increased requirements for refractoriness, chemical stability, etc.

In accordance with GOST 5040-68, maximum temperatures were established for the melting chamber when using aluminosilicate and silica thermally insulating products in the working (unprotected) furnace lining, not subjected to the action of molten slags, metal, glass, ashes, etc. (Table 53).

Table 53 Таблица 53

A Предельная температура применения алюмосиликатных и динасовых легковесных огнеупоров

| Product type | Product marking | Температура применения, °C, не выше B |
|---|---|---|
| Fireclay and semiacid | ШЛА-1,3 ShLA | 1400 |
| | ШЛБ-1,3; ШЛБ-1,0 | 1300 |
| | ШЛБ-0,9 | 1270 |
| | ШЛБ-0,8 ShLB | 1250 |
| | ШЛБ-0,6 | 1200 |
| | ШЛБ-0,4 | 1150 |
| Kaolin | КЛ-1,3 KL | 1400 |
| | КЛ-0,9 | 1400 |
| High alumina | ВГЛ-1,4 VGL | 1600 |
| | ВГЛ-1,3 | 1550 |
| | ВГЛ-1,0 | 1400 |
| Silica | ДЛ-1,4 DL | 1550 |
| | ДЛ-1,2 | 1550 |

A - Maximum temperature for use of aluminosilicate and silica lightweight refractories

B - Use temperature, °C, not exceeding

In the presence of molten agents in the melting chamber of the furnace, refractory thermally insulating products are used for the intermediate (protected) insulation at the maximum permissible temperatures, indicated in Table 53.

Here the possibility should be taken into account of interaction at the contact of the working layer with the layer of thermal insulation.

Lightweight aluminosilicate refractories find wide use in furnace construction and other fields of technology, and they are the most popular and universal porous materials with a wide assortment of products with respect to apparent density, structure and overall dimensions. They are used for the working and intermediate linings at various temperatures up to 1550-1600°C.

Aluminosilicate, specifically fireclay, materials of various types were tested as open and intermediate insulation in steam boilers, electric furnaces, forge furnaces, etc. (6).

It was established that the principal reason for failure is insufficient thermal stability and the presence of noticeable reheat shrinkage.

Considerable experience has been accumulated with respect to the service provided by aluminosilicate porous refractory materials in various fields of technology. They are used successfully in blast furnace plants for the thermal insulation of air heaters and hot blast air ducts, in rolling mills for the thermal insulation of soaking pits, and for the lining of walls and roofs in electric furnaces - heating, annealing, heat treating (7, 15, 18). Fireclay lightweights are suitable for the thermal insulation of any hot surfaces not in contact with the melts (39) in the absence of sharp thermal shocks (15); in the last case, products with combustible admixtures can be used.

Fireclay materials serve successfully in the lining of electric furnaces, in the roofs and walls of various heat treating furnaces, boiler furnaces, and in furnaces of all designs (periodic, gas chamber kiln, annular and tunnel) intended for firing ceramic and refractory products (241).

The ~~application~~ use of lightweight fireclay refractories for the insulation of tuyere nozzles in blast furnaces instead of slag wool and asbestos made it possible to raise ~~the temperature of~~ the blast temperature and thereby to intensify the blast furnace process (164).

An excellent thermally insulating material is the so-called ultralightweight (6), which is used for the thermal insulation of furnaces in areas where especially great demands are made on the material with respect to its thermal insulating capacity.

It was established that ultralightweight is suitable for lining furnaces operating ~~it~~ in carbon-bearing atmospheres, specifically in endogas containing 40% $H_2$, 20% CO, and $CO_2$ and $CH_4$ as impurities, balance $N_2$ (173). After 500 hrs. service, there were no signs of failure in the ultralightweight at the same time as the normal fireclay brick and the BL-1,0 fireclay lightweight failed after 50 hrs. in the furnace at 550°C on account of the formation of sooty carbon as a result of the catalytic action of iron impurities in the reaction

$$2CO \rightleftarrows CO_2 + C; \quad CH_4 \rightleftarrows 2H_2 + C.$$

A fireclay-talc lightweight having increased strength turned out to be even more stable, which makes it possible to use it also in the loaded portions of the lining, where the heaters are installed.

Foamed lightweight fireclay materials with increased strength are used for the insulation of equipment for the production of manufactured liquid fuel at a service temperature of up to 500-600°C and pressure up to 700 atm (15).

Very effective thermally insulating materials are various lightweight concretes (244, 245), specifically fireclay-vermiculite and based on perlites; they can be used at temperatures up to 1100°C in place of lightweight fired refractories.

Lightweight fireclay materials cannot be used in high-temperature units.

A high-alumina lightweight (50) successfully passed the tests in the lining of the furnaces of the auxiliary steam boilers on tankers heated by fuel oil. The temperature of the fuel spray was 1500°C; besides this, soot from the fuel oil and intense vibration affected the refractory. The lining was in service 14 months including 6000 hot hours. During the same period, the boiler lining, equipped with dense semiacid brick, was replaced twice (47).

Also an effective material is a high-alumina lightweight made from a kyanite-sillimanite concentrate (184), which can be used at temperatures of 1500-1530°C in the lining of various furnaces, in the furnaces of marine boilers heated by fuel oil, and in the hot blast air lines of blast furnaces. The sillimanite lightweight is successfully used for lining the intermediate layer in highly stressed high-temperature glass-making furnaces.

Silica lightweight is used for the lining of furnace walls, roofs and the insulation under the hearth. The greatest effect is provided by the use of porous silica in heating, forging and heat treating furnaces and also in periodic and gas chamber furnaces for firing silica, fireclay and other ceramic products (15).

The basic lightweight materials are used to a considerably smaller extent than the aluminosilicate and silica ones. It is shown in the patent literature (102) that porous materials based on magnesite, chromite, forsterite and magnesium spinel, and made by the method of introducing a combustible admixture (graphite), are recommended for use as thermal insulation in open hearth furnaces, mixers, etc.

Lightweight forsterite, made from dunite, magnesite and quartz with the introduction of combustible admixtures (coke), can be used in the intermediate layer of insulation in contact with magnesite, magnesite-chromite and chrome-magnesite products at a temperature at the junction of up to 1550°C, specifically as the inner layer of insulation in furnace cars in high temperature furnaces (202).

Porous highly refractory corundum materials, according to the unanimous opinion of all the investigators, can serve successfully under normal conditions (oxidizing atmosphere, absence of substantial loads, etc.) all the way up to 1750-1850°C (20, 21, 46, 214).

High porosity corundum is an effective thermally insulating material (90, 97). Having a low thermal conductivity at a low apparent density, foamed corundum is simultaneously characterized by high refractoriness, chemical inertness, and excellent electrical insulation properties, which permits its use as a high-temperature thermal insulation under conditions of the action of various chemical reagents in oxidizing and reducing media.

Foamed corundum is a strong material, does not crumble and does not make dust. This makes it possible to use it in vacuum technology in the form of molded parts or as packing with grains from 0.5 to 20 mm in size. The material was successfully tested as thermal insulation in vacuum furnaces with tungsten heaters, in other high-temperature electric furnaces and also in platinum baths for the production of glass fibers. Foamed corundum is recommended for use in heating units with a high ~~working~~ operating temperature, where good thermal and electric insulation, low thermal capacity, and chemical stability are required. Besides this, foamed corundum is used for work in vacuum.

Corundum foamed ceramic, obtained from alumina by the chemical gas formation method (89), was successfully tested in the lining of the melting chamber of a periodic high-temperature box furnace Type SNO-3-45-2/16 with molybdenum disilicide heaters. The corundum lightweight was successfully tested in service in an electrical furnace at 1600 C in an oxidizing atmosphere (92). Materials of a similar type, processed in hydrochloric acid with the aim of raising the $Al_2O_3$ content up to 99%, can also be used at 1750°C (214).

Foamed corundum materials, obtained by chemical swelling, can be used at 1650°C according to foreign data (96), including systems with ~~moving~~ flowing hot gases.

From corundum there are prepared by various methods hollow spheres, from several micrometers in diameter to several millimeters, which are recommended for packing insulation to a temperature of about 1850°C (21). The indicated spheres can be also used as filler for bonded products. Corundum lightweight Mark Al frax B-1, consisting of molten hollow spheres of $Al_2O_3$ and a ceramic bond, is characterized by a low heat capacity and good thermal insulation properties at very high temperatures, can be in contact with the combustion products of any fuels except heavy oils to 1800°C, is inert to the majority of acid and basic materials; it is recommended as a wall and roof material in periodic and continuous furnaces, in gas generators and in various resistance furnaces (212).

For high-temperature thermal insulation in the working linings of the walls and roofs in periodic and continuously acting furnaces at temperatures of 1750-1800°C, a semilightweight corundum refractory is recommended with an apparent porosity of about 40% (46).

The lightweight material "Insulpur", consisting of 95% $Al_2O_3$ and 5% CaO, can be recommended for service at a high temperature in an atmosphere of pure dry hydrogen (246).

A material of analogous composition based on alumina, chalk and sawdust as the combustible admixture was used successfully in a bell furnace for annealing transformer steel in a dry hydrogen atmosphere (213). Under these conditions, the basic and aluminosilicate materials failed as a result of the reduction of the iron and silicon oxides. In 2.5 years of operation of the bell furnace, the corundum lightweight underwent practically no changes.

A highly effective thermally insulating material is the so-called foamed alumina cement, which does not require high-temperature firing (97). It is recommended for use in aircraft power plants, guided missiles and other devices operating under conditions of high temperatures, loads, high gas velocities and aerodynamic vibrations. The use of such a cement raises the thermal efficiency of the engine, lowers the cooling requirements for it, and improves the operating characteristics of the power plants.

According to the efficiency index for thermal insulation (product $\lambda\gamma$ ), the cement exceeds almost twice, for example, a material based on crushed corundum with a phosphate bond.

Porous zirconia refractories, on account of the low thermal conductivity of $ZrO_2$, are especially efficient thermally insulating materials up to 2200-2300°C. Products based on the dioxide of zirconium, obtained by the foaming method, are recommended for service in an atmosphere of air, nitrogen, hydrogen and in vacuum at 2315°C; in a reducing atmosphere in the presence of carbon at 1650°C; in contact with SiC at 1200°C; in contact with $SiO_2$ and $Al_2O_3$ at 1650°C (223). The data presented for vacuum appear to be somewhat overstated since vaporization starts to be noticeable at 2300°C for the highly porous material.

More realistic is a temperature of 2000 C indicated by A. Pirogov (215). For zirconia lightweights, made by the method of introducing combustible admixtures, he recommends a service temperature of 1800°C for unloaded elements of the lining on account of the reduced deformation temperature under load (216).

The ~~the~~ maximum service temperature for porous zirconia materials depends to a large extent on the degree of purity of the initial zirconium dioxide. At a temperature higher than 2000°C, only highly pure materials can apparently be used, with a $ZrO_2$ content ( without taking the stabilizer oxide into account) of more than 99%.

Other materials are sometimes also used as thermal insulation. A high-temperature thermally insulating material is a lightweight obtained by the vacuum-thermal swelling of various minerals of the quartz group (opal, chalcedony)(33). Products based on quartz are used, for example, in radar equipment, which is associated with the low dielectric losses of swelled siliceous grains (tan $\delta < 0.002$) (199).

Materials based on $SiO_2$, MgO, $Al_2O_3$ and $ZrO_2$ and bonded with silicates, phosphates and oxychlorides are used as thermal insulation in rocket equipment (86).

In the absence of oxidizing agents, cellular carbon materials (in a reducing atmosphere to 3315°C) and porous chighly refractory materials based on silicon carbide can serve as efficient thermal insulators (104, 123). According to Carborundum Co. data, foam carborundum can be used to 2200°C in an inert atmosphere, but to 1650°C in an oxidizing one. Apparently, the last figure refers to short-term service since a porous material based on SiC cannot be used for a prolonged time in an oxidizing atmosphere. This circumstance is considered in (232) as applied to a siliceous bond, which is recommended for use in neutral and reducing atmospheres at 1600°C under a stress of 1 $kg/cm^2$ and at 1700-1800°C at a stress of less than 1 $kg/cm^2$. The possibility is also reported of using the material in vacuum at a temperature below the temperature of noticeable evaporation of silican carbide.

Fibrous materials, whose production technology is not considered in the present work, provide efficient thermal insulation. Fibrous materials, made from refractory raw materials, can be used at very high temperatures unlike ordinary glass fibers.

In the literature (247-253) there is described the use of various fibrous materials, known under the names "Fiberfrax", "Kaowool", "Triton Kaowool", "Refrosil" and others, of kaolin and mullite composition based on the pure oxides $SiO_2$ and $ZrO_2$, and also on graphite.

Fibrous refractory materials, first intended primarily for ~~cosmic~~ space technology, at present are finding wider use in the metallurgical, gas, ceramic, glass and other branches of industry in the form of paper, tapes, films, cloth, batting, cardboard, plates, mats, blocks, tubes, etc.

Fibrous material of kaolin composition "Kaowool" is used for the trailing parts of rocket engines, guided missiles, for the thermal insulation of furnaces and high-pressure steam turbines, and the manufacture of refractory structures. Products based on "Kaowool" fiber retain their strength and elasticity to 1100°C, at the same time as slag wool is effective only to 650°C and glass wool to 540°C (274).

The fibrous aluminosilicate material "Triton Kaowool" can be used at 1260°C for the lining and thermal insulation of furnaces, for the combustion chambers of furnaces, in gas and steam turbines, in jet engines, in equipment for glass tempering, and for the production of furnace accessories and seal packing.

In a number of cases, fibrous and wool-like materials are successfully replacing lightweight refractories in metallurgy, especially in places where a complicated configuration of the thermal insulation is required (254, 255).

The fiber "Fiberfrax" of mullite composition retains the thermoinsulating properties to 1300°C, with softening occurring about 1700°C (251). It is used in various fields of technology, where a light, strong, fibrous material with low thermal conductivity is required (253), for example, for aircraft and rocket engines, lining of tubes, channels, pouring ladles, and ingot molds used for transporting or pouring such metals as aluminum, magnesium, brass and bronze, which do not wet and destroy the aluminosilicate fiber.

The siliceous fibrous material "Refrosil", containing 99% $SiO_2$ and developed by the firm HITCO (California, USA), is used for thermal insulation at temperatures up to 1450°C. Polycrystalline fiber based on $ZrO_2$, made by the same firm, is suitable for use at temperatures up to 1650-2200°C (250).

## Use of Porous Materials as Thermal Protection

The problem of thermal protection for equipment against heat coming from without is not new but it became especially acute in connection with the return to earth of ~~cosmic~~ space objects entering the earth's atmosphere at tremendous speed, exceeding the speed of sound many times. In the dense layers of the atmosphere, the surface of the equipment is heated to temperatures exceeding 2000°C. E. Shtraus (201) shows that the temperature at the surface of the shell of the space ships can be from 1650 to 2200 C; according to the data of V. Veler (258), the surface of rockets and other flying vehicles is heated to 1400–2200°C in an interval of about 90 min.

Various porous refractory materials based on pure refractory and highly refractory oxides and silicon carbide have been tested as thermal protection materials (74, 86, 100, 201, 220, 221, 256, 257, 259, 260), specifically foamed ceramics based on $SiO_2$ (fused quartz), $Al_2O_3$, MgO, $ZrO_2$, $ZrSiO_4$, SiC and various fibrous materials. The thermal protective materials must resist high temperatures and high temperature gradients, i. e. must be refractory and thermally stable, have sufficient strength under conditions of aerodynamic loads and vibrations, and be characterized by low coefficients of thermal conductivity and diffusivity, i. e. have a unique complex of properties, which not one of the known types of porous ceramics has in full measure.

Therefore the aim is to select such materials and thermal protection design, ~~as~~ which would be in a position to release the absorbed heat back into the surrounding atmosphere in the form of radiation (258), in order that the radiative capacity of the surface of the material would be not ~~les~~ less than 0.6 of the black body radiation. To increase the degree of radiation at the surface of porous ceramic materials, ~~by the method of~~ a coating that increases the degree of blackness is applied by the methods of dipping, spraying and slushing. In applying, with the use of a phosphate bond, coatings of the oxides of cobalt, nickel and chromium and also of silicon carbide and molybdenum disilicide, the degree of radiation is increased to 0.9. For the efficient use of foamed ceramics as thermal protection of space ships returning to earth, it is necessary to apply a thermal reflection layer to its surface (259). As reported by A. Allen (74), an insulating material based on zircon (54-75% $ZrSiO_4$) with a silicate bond, having high reflective power in the infrared region, was developed at the behest of the American national committee on aeronautics and space investigation.

Use as thermal protection in rocket and aviation technology was also found for porous ceramic and fibrous materials impregnated with organic and inorganic substances which create at high temperatures an ablati~~on~~ve or cooling effect upon the vaporization of the injected compound from the pores (257). It was established that in the thermal protective layer the silicate bonds are more stable than the phosphate ones while impregnation of the pores with organic compounds is more effective than with inorganic ones (ZnS, $NH_4Br$).

Tests were made of the design of ~~the~~ a protective layer of foamed ceramic based on SiC, $SiO_2$, $Al_2O_3$ and $ZrO_2$ with an apparent density, respectively, of 0.32, 0.34, 0.52 and 0.73 g/cm$^3$, i.e. with a porosity of 85-90%, impregnated with organic resins (201, 221).

Filling the pores with resin noticeably (by 25-40%) raises the apparent density of the ceramic but at the same time the compressive strength increases sharply (3.5-9 times!), which is important since the high-porosity foamed ceramic, especially of fused quartz and silicon carbide, has insufficient mechanical strength.

In the proposed design, the pores of the refractory shell are filled with substances that sublimate or dissociate at high temperatures, on account of which the impregnated foamed ceramic thermal protection, upon entry into the dense layers of the ~~atmosphere/surrounding~~/atmosphere, returns to the surrounding space a considerable portion of the acquired heat. As a result, the temperature of the protected surface increases relatively slowly.

For reliable thermal protection, the ceramic refractory shell of the heat shield must not change its shape, be subjected to destructive erosion or to melt. The latter can occur if the temperature of kinetic heating exceeds the melting or dissociation temperature of the ceramic. It has been calculated (201) that for this to happen, the heat flux upon the return of the space ship must exceed 177-545 kcal/$m^2$·sec (the calculations are made in conformity with the melting or dissociation temperatures of a foamed ceramic based on SiC, $SiO_2$, $Al_2O_3$ and $ZrO_2$). To raise the strength of a foamed carborundum ceramic, it was coated with a thin layer of zirconium dioxide (259). The protection of foamed carborundum ceramic is also reported in (258). The ceramic was impregnated with a thin layer of a mixture of $ZrO_2$ and $H_3PO_4$ and after impregnation it was subjected to a two-hour heat treatment at 480 C. Tests on the ceramic based on SiC were conducted at temperatures of 1860 and 1920°C, on $Al_2O_3$ at 1815°C and on $ZrO_2$ at 2200°C.

The thermal tests for evaluating the strength of various materials were conducted with the aid of oxy-acetylene and plasma torches on specimens 75 mm in diameter and 19 mm thick held at a temperature of 2480°C for five minutes, or on spherical specimens imitating the nose of the space ship, by directing a flow of hot gases from the nozzle (201). The best results were obtained for a foamed ceramic from $Al_2O_3$ and SiC.

To evaluate the structural strength, the specimens were quickly heated by a gas torch to 1480-1650°C with the noise at a level of 150 db and with the pressure at 1.8 t/$m^2$. For the resin-impregnated foamed ~~ceramic~~ $Al_2O_3$ ceramic, heating the opposite side for 10 min in this case amounted to only 260 C and no surface erosion was observed. Good results were observed also for large noses 330-390 mm in diameter, made from impregnated foamed carborundum ceramic and tested for 10 min at 1900°C.

Before assembling, the foamed ceramic is carefully processed (220) and it is applied to the object with the aid of silicone rubber or a cast slip and cellular layer of aluminum foil with a fibrous insulation (259). Various cellular structures, epoxy resin and also cement can be used for this purpose (201, 258).

Along with the their good qualities, porous refractory materials used for the thermal protection of spacecraft also have shortcomings, the principal one being the large spread in the properties, connected with the fluctuation of the apparent density and the nonuniformity of the structure. Therefore the most important problem is to ensure the constancy of the physical and mechanical properties of the ceramic being used.

## Application of Porous Refractory Materials Associated with Their Permeability

Permeability with respect to liquids and gases is one of the most important properties of porous ceramic materials (12-14, etc.)

The most important fields of use for permeable ceramics are filtration, aeration, distribution of gases, diffusion, electrolysis, etc. Usually these processes take place at room temperature or slightly above but in a number of cases, and these situations are now met more frequently, they must be conducted at very high temperatures and besides in corrosive media; in these cases, permeable materials are used that are refractory and corrosion-resistant (120).

There are a number of reports about the use of porous permeable materials in metallurgy, new fields of energy, etc. Thus porous ceramic diaphragms are used for blowing steel with gases through the bottom of the ladle with the aim of purifying the metal from harmful gases and nonmetallic inclusions (261). The structure of the diaphragms must be such that they are permeable to gases and impermeable to the metal. Blowing the steel with gases can be done both in air and in vacuum (262-264). For example, for blowing steel with argon, porous diaphragms based on fused magnesite were used but materials that are not wet by metals and slags, for example graphitic fireclay, are considered more promising.

In recent years there has again been a return to thermal elements — to electrochemical generators, whose advantage lies in their high efficiency, reliability, and simplicity of design, which results in their use as airborne power plants for space ships and satellites (13, 265-267). For this purpose, porous cermets (13), ceramic matrices based on periclase in whose pores appropriate electrolytes are present, and porous carbon materials (124) are used as electrodes.

An important field of application for porous refractory materials is the filtration of hot gases and melts. For example, porous materials made from the carbides and borides of the transition metals make it possible to filter the melts of some metals, alkalies and other corrosive media (238, 268).

Filters based on corundum can also be used for cold filtration and at high temperatures of acids, alkalies and other corroding liquids, and these filters also withstand high pressures (239, 269). The action of many corroding agents is resisted well by porous self-bonded silicon carbide, which is used in atomic reactors and for the filtration of corrosive media (123).

For the filtration of hot gases, liquids and metals, use is made of the abovementioned fibrous materials, "Refrosil" and "Fiberfrax" (250, 251); the latter can also find application for the purification of hot gases in atomic power stations from radioactive particles and in general of air from solid particles at high temperatures (253).

Porous permeable materials can be used not only for the uniform distribution and delivery of gases and liquids but also for cooling hot surfaces, passages, volumes, etc., by the method of delivering the coolant through the porous wall in the form of gases or liquids. As an example, one can point out the promising use of porous refractory materials for the wall linings of combustion chambers, which can be cooled by the transmission of a gaseous or liquid coolant (238). In this case, the temperature of the working gases can be raised and thereby the efficiency of the gas turbines and jet engines. On the principle of the uniform delivery of gases and liquids are also based the implementation of fluid-bed reactions, pneumatic transport, mixing of liquids and gases, cooling of hot materials and many other processes.

Porous materials are widely used as catalyst supports and in particular various kinds of corundum materials are used for this purpose, having high chemical inertness and by necessity a high specific surface of the order of tens of $m^2/g$ (73). Corundum, mullite, siliceous, cordierite and other porous ceramic materials (269), and also fibrous materials (253) find application in in electrical engineering as electric resistance materials for various purposes.

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